

# CARBON NANOTUBE BASED PYROPHORIC SUBSTRATES WITH A TUNABLE RESPONSE FOR INFRARED COUNTERMEASURES

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## ABSTRACT

In recent years there has been a significant effort to exploit the pyrophoricity of various metal nanoparticles for Department of Defense (DoD) applications. Materials based on iron (Fe) are highly desirable because i) pyrophoric iron particles can be easily generated by reduction of inexpensive Fe-based precursors under hydrogen at relatively low temperatures 350-600°C and ii) the oxidation product is environmentally benign.

In this work we report the fabrication and characterization of porous self-supporting substrates based on multi-walled carbon nanotubes (MWNTs) and inclusion of pyrophoric  $\alpha$ -Fe nanoparticles. The substrates were fabricated by pressure filtration of aqueous dispersions of carbon nanotubes and iron oxide nanoparticles followed by reduction under hydrogen. The temperature response was characterized with both an IR-pyrometer and a thermal camera. MWNT-Fe substrates consistently showed thermal responses of  $\sim 500$  °C sustained for 5 seconds depending on iron concentration. It was found that the temperature response and sustenance could be tuned in the range of 500 °C to  $> 900$  °C with the addition of a secondary fuel such as Al or TiH<sub>2</sub>.

**Keywords:** *pyrophoric nanoparticles, carbon nanotubes, IR countermeasures.*

## 1. INTRODUCTION

Over the past decade much of the research conducted by the Department of Defense (DoD) has focused on the use of various nanoparticles to improve current technologies and better protect our soldiers in the field. Current infrared decoys for the protection of manned and unmanned aircraft are based on many different material types depending on their mission. These materials range from pyrophoric porous iron foils to MTV flares. The currently used pyrophoric porous iron foils are fabricated by the formation of FeAl or FeZn alloy foil annealed at high temperature followed by leaching of the Al or Zn using warm NaOH solution (1-3). An optimum new pyrophoric material would meet

the following criteria: 1) have an environmentally friendly production method, 2) is environmentally benign after reaction and 3) allow for the infrared response to be tuned based on the end use.

Many different nano-size metals are pyrophoric when exposed to air but iron (Fe) is a readily available metal that forms an environmentally benign oxide. Pyrophoric Fe-nanoparticles can be produced by several methods, including thermal decomposition or plasma synthesis from Fe-precursors, selective leaching of a secondary metal from an alloy (e.g. FeAl) or the reduction of Fe-precursors such as iron oxide or oxalate in a hydrogen rich environment(4-6). It has been previously reported that highly porous alpha-iron nanoparticles are pyrophoric when exposed to ambient air generating a temperature response greater than 900°C. Recently it was shown that porous pyrophoric substrates were fabricated by the reduction of Fe based sol-gel coatings(6, 7). While these methods of producing pyrophoric nanoparticles have been very successful the implementation of such particles for IR countermeasures remains problematic due to minimal adhesion of such nanoparticles to the substrate surface after reduction. To be able to effectively implement such materials for IR countermeasures a new method of effectively adhering or containing these nanoparticles within the substrate is necessary.

In this contribution a unique method for the fabrication of porous self-supporting pyrophoric substrates that meets the previously set forth criteria is reported. Self-supporting substrates were fabricated by vacuum filtration of aqueous dispersions of multi-walled carbon nanotubes and iron oxide nanoparticles. The incorporation of iron oxide nanoparticles into the porous carbon substrate produces an iron nanoparticle infused substrate which is pyrophoric after reduction in a hydrogen environment. As previously stated, pyrophoric iron nanoparticles can be generated by the reduction of iron oxide nanoparticles in a hydrogen atmosphere at temperatures between 350-600°C. Multi-layer and single-layer substrates were tested.

It was found that multi-layer substrates generate a maximum surface temperature of 575°C for several

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seconds for an iron/carbon ratio of 1:1 (wt). Single-layer substrates performed similarly. The pyrophoric response can be tuned by configuration, adjustment of the iron/carbon ratio and/or the addition of other materials that react with either atmospheric oxygen/nitrogen or the oxidation products (e.g.  $\text{Fe}_2\text{O}_3$ ). Examples of potential reactive materials include Al, B, Si and  $\text{TiH}_2$ . In the case of Al as the secondary fuel pyrophoric oxidation of the iron nanoparticles ignites the thermite reaction between the oxidation products and Al generating temperatures well over  $900^\circ\text{C}$ .

## 2. EXPERIMENTAL

### 2.1. MATERIALS

The carbon nanotubes used were Multi-walled carbon nanotubes (diameter = 8-15 nm) purchased from Cheap Tubes Inc. Both NanoArc cosmetic grade ( $35 \text{ m}^2/\text{g}$ ) from Alpha Aesar and  $\alpha$ -iron oxide nanoparticles ( $20 \text{ m}^2/\text{g}$ ) from Nanostructured and Amorphous Materials, Inc. were used. Attrition milling was used to increase the surface area of the  $\alpha$ -iron oxide nanoparticles to  $35\text{--}44 \text{ m}^2/\text{g}$ . The secondary fuels that were used were 80 nm aluminum (NovaCentrix), 2-4  $\mu\text{m}$  aluminum (Valimet), and  $8\mu\text{m}$   $\text{TiH}_2$  (Chemetall). Nanospense AQ (NanoLab) was used as the dispersant.

### 2.2. CARBON NANOTUBE DISPERSION

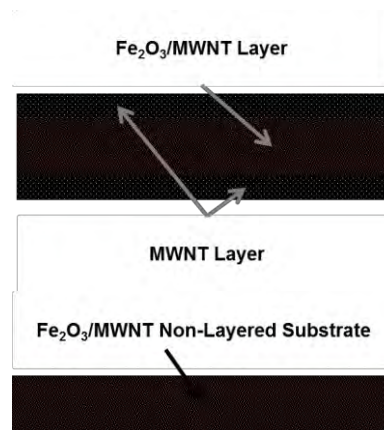
In order to fabricate self-supporting substrates of carbon nanotubes the nanotubes must be well dispersed since nanotube agglomerations limit their use in acting as porous supports for the iron oxide nanoparticles. In this work good dispersions were attained using  $\sim 120 \text{ mg}$  dispersant/100 mg CNTs in 100 mL water followed by probe sonication with a Sonics VCX130 for 15 minutes at 60 % amplitude pulsed for 30 seconds ON/OFF. After sonication the sample is used as is or separated into appropriate volumes depending on the configuration of the desired substrate.

### 2.3. NANOPARTICLE DISPERSION

Depending on substrate configuration either an iron oxide nanoparticle suspension was made or the nanoparticles were directly added to the pre-dispersed MWNTs. The concentration was kept at  $1 \text{ mg}/1 \text{ mL}$  water for the individual iron oxide suspension. In either case, probe ultrasonication for 15 minutes at 60 % amplitude pulsed for 30 seconds ON/15 seconds OFF was used. If aluminum was used as the secondary fuel 2.5 wt% of ammonium dihydrogen phosphate was added to the water to protect the aluminum from oxidation prior to addition to the suspension.

## 2.4. SUBSTRATE FABRICATION

In this research two different types of substrates were generated. They will be referred to as multi-layer or single-layer for the remainder of this paper and are depicted in Figure 2.4-1. For the majority of experiments pressure filtration was used with filter pressures varying from 10-50 psi. 47 mm polyamide Whatman filters with  $0.2 \mu\text{m}$  pore size were used. After filtration the substrates were removed and allowed to dry at room temperature. In the case of Al as a secondary fuel, the substrates were dried in a vacuum oven at  $100^\circ\text{C}$  for 2-3 hours to minimize long term exposure to moisture.



**Figure 2.4-1: Diagram showing the two different substrate configurations; multi-layer (top), single-layer (bottom).**

#### 2.4.1. MULTI-LAYER SUBSTRATES

The multi-layer substrates consist of three distinct layers. These layers result from filtering: 1) MWNT suspension, 2) MWNT/ $\text{Fe}_2\text{O}_3$  or  $\text{Fe}_2\text{O}_3$  suspension, 3) MWNT suspension and 4) 50-200 mL of water to remove residual dispersant.

For the substrates that contain a secondary fuel such as Al or  $\text{TiH}_2$  the fuel was mixed in step 2 of the filtration process.

#### 2.4.2. SINGLE-LAYER SUBSTRATES

The single-layer substrates were prepared by filtration of the MWNT/iron oxide suspension followed by washing. If the substrates contain a secondary fuel it is mixed with the MWNT and iron oxide nanoparticles as described above.

## 2.5. IRON OXIDE MILLING

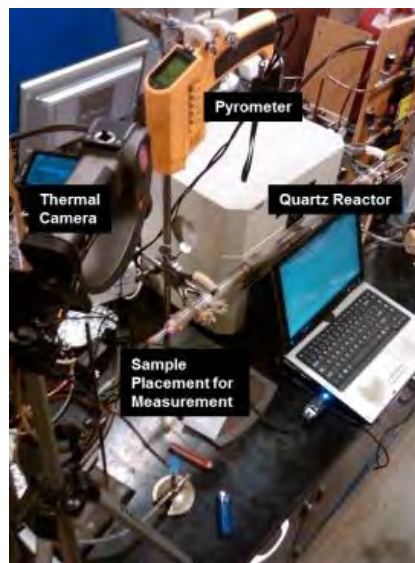
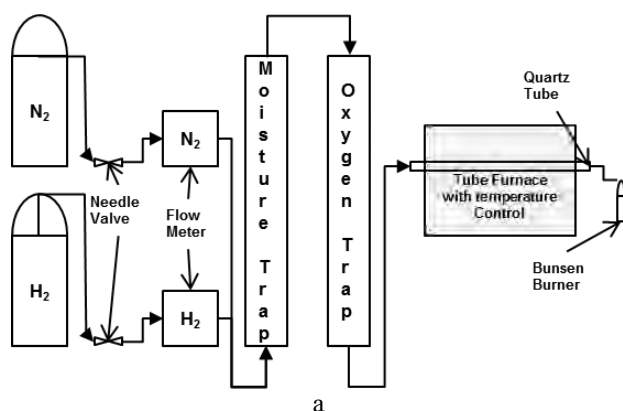
The alpha-iron oxide powder purchased from Nanostructured and Amorphous Materials had a much lower specific surface area which resulted in difficulties maintaining the dispersion during filtration. To increase the specific surface area of the iron oxide powder it was milled in a lab scale attrition mill (Model 01HDDM purchased from Union Process) using 0.4 mm zirconia grinding media. The sample was milled in water for 6 hours. This milling increased the specific surface area up to 44 m<sup>2</sup>/g and solved the dispersion problems.

## 2.6. SUBSTRATE REDUCTION

The procedure for the reduction of the iron oxide nanoparticles to pyrophoric  $\alpha$ -Fe nanoparticles was as follows:

- The sample was placed in a tubular quartz reactor (Tube diameter = 0.844 inches, length = 27 inches) in a split tube furnace.
- The reactor was flushed with ultra-high purity (UHP) nitrogen to remove any oxygen.
- The reactor was then flushed with hydrogen for 5 minutes and then heated to between 400-550°C.
- Once the desired temperature was reached the temperature was held constant for 25-60 minutes.
- The reactor was removed from the split tube furnace and allowed to cool to room temperature under hydrogen atmosphere.
- After flushing the reactor with UHP nitrogen the sample was then removed from the reactor and the thermal response was recorded using a thermal camera and infrared (IR) pyrometer.

A schematic and photograph of the reduction setup is shown in Figure 2.6 1.



**Figure 2.6-1: a) Schematic of reduction setup, b) Photograph of reduction setup with thermal camera and IR pyrometer for thermal response measurement.**

## 2.7. THERMAL RESPONSE CHARACTERIZATION

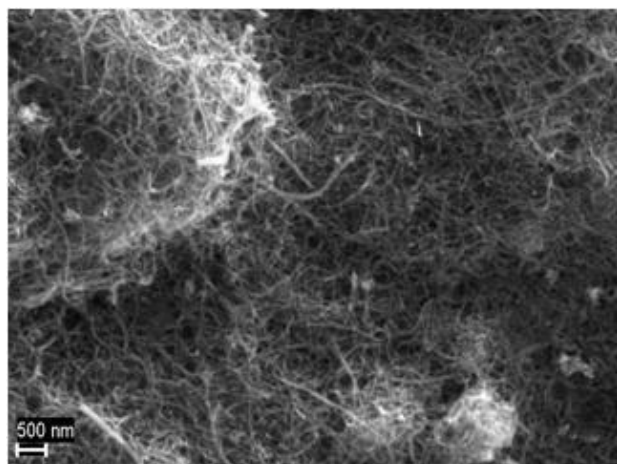
The thermal response of the porous self-supporting substrates was conducted using a thermal camera with a temperature range of -150 to 1000°C (Model T2i purchased from Infrared Cameras, Inc.) and an infrared (IR) pyrometer with a temperature range -30 to 900°C (Model 574 purchased from Fluke). Figure 2.6 1 shows the placement of the thermal camera and IR pyrometer used for recording the thermal response of the substrate when exposed to ambient air after reduction.

## 3. RESULTS AND DISCUSSION

### 3.1. SUBSTRATES

In this work we are interested in minimizing the thermal losses from the porous substrate, yet it must perform two functions; be structurally stable and effectively contain the iron oxide nanoparticles. Therefore, it was first necessary to determine the minimum thickness of the MWNT layer which is self-supporting. This indicates that it can be removed from the filter with tearing and acts essentially as a sheet of paper. Suspensions containing 20 to 60 mg MWNTs were filtered using both vacuum and pressure filtration and “peeled” off the filter to determine if they were self-supporting. It was found that 20 mg of MWNTs was necessary for vacuum filtration while for pressure filtration 40 mg MWNTs was necessary. The minimum

thickness for both was around 100  $\mu\text{m}$ . This was consistent with reports for the commercially available buckypaper(8). A scanning electron image of the top of a pressure filtered substrate is shown in Figure . The small particles that can be seen are residual iron/cobalt synthesis catalyst used for MWNT synthesis. These substrates have porosities on the order of 50% and as shown the intertwined nature will aid in iron oxide nanoparticle retention.



**Figure 3.1-1: SEM image of MWNT substrate generated using 40 mg MWNT using a filtration pressure of 20 psi.**

Both multi- and single-layer substrates were fabricated using the methods described previously. Multi-layer substrates essentially sandwich the iron oxide nanoparticles within two identical layers of MWNTs. A typical multi-layer substrate with 200 mg of 20-40 nm  $\text{Fe}_2\text{O}_3$  nanoparticles/60 mg MWNTs in the middle layer at a filtration pressure of 20 psi is shown in Figure 3.1-2.

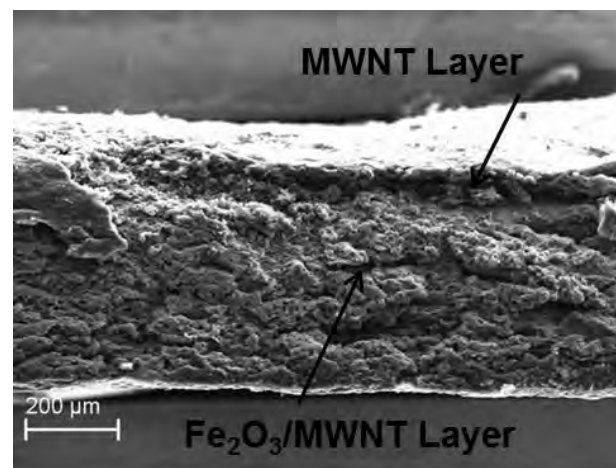
During reduction hydrogen must diffuse through the carbon nanotube layers to reduce the iron oxide to pyrophoric iron. Likewise, air must diffuse through the carbon nanotube layers after reduction to result in the desired pyrophoric response. This is the primary reason for minimizing the MWNT concentration. In addition, MWNTs have a high thermal conductivity which may result in dissipation of the thermal energy at a rate that is undesirable. Preliminary substrate fabrication focused on those in which solely  $\text{Fe}_2\text{O}_3$  occupied the middle layer, however after drying delamination of the layers was observed. Therefore all additional multi-layer substrates were fabricated with the middle layer consisting of suspensions of  $\text{Fe}_2\text{O}_3$  and MWNTs.

Scanning electron microscopy images of the substrates revealed that it was quite difficult to

differentiate the MWNT and  $\text{Fe}_2\text{O}_3$ /MWNT layers from each other as shown in Figure 3.1-3. Typical thicknesses of the substrates range from 100-500  $\mu\text{m}$ . As shown in Figure 3.1-4 the middle layer shows good retention of the iron oxide nanoparticles within the pores of the nanotube mat.



**Figure 3.1-2: Photograph of multi-layer substrate with 200 mg of 20-40 nm  $\text{Fe}_2\text{O}_3$  nanoparticles in the middle layer at a filtration pressure of 20 psi.**

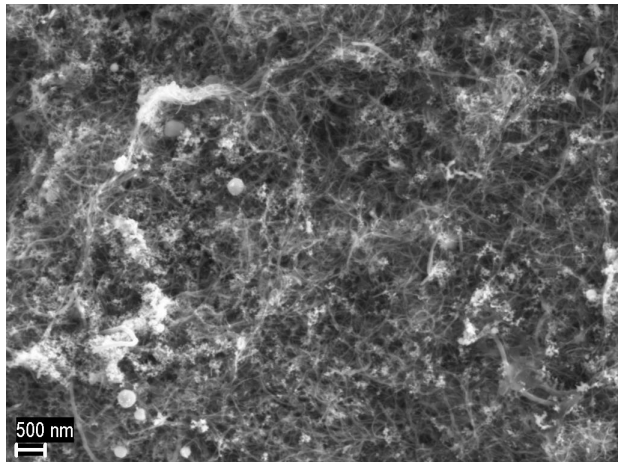


**Figure 3.1-3 SEM of multi-layer substrate with 100 mg of 20-40 nm  $\text{Fe}_2\text{O}_3$  nanoparticles in the middle layer.**

Single-layer substrates were fabricated to determine i) the effect hydrogen/oxygen diffusion through the carbon nanotube layer had on the pyrophoric response and ii) the minimum quantity of MWNTs that was necessary to provide a self-supporting substrate while still providing the desired thermal response. Typical thicknesses of these substrates were 100-500  $\mu\text{m}$ .

We have previously measured the thermal response of 200 mg of loose pyrophoric iron produced by  $\text{H}_2$

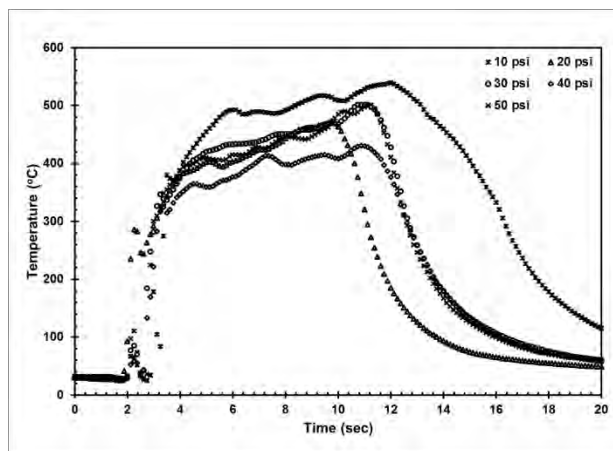
reduction of the same  $\text{Fe}_2\text{O}_3$  powder and observed a thermal response of greater than  $900^\circ\text{C}$  when exposed to ambient air. We anticipated a lower thermal response due to the presence of the MWNTs but initially had no prediction of what that temperature might be. We first considered the multi-layered substrates with 40 mg total MWNTs and 100 mg  $\text{Fe}_2\text{O}_3$ . As shown in Figure 3.2-1 it was observed that there was a minimal difference in the thermal response when filtration pressures exceeded 10 psi.



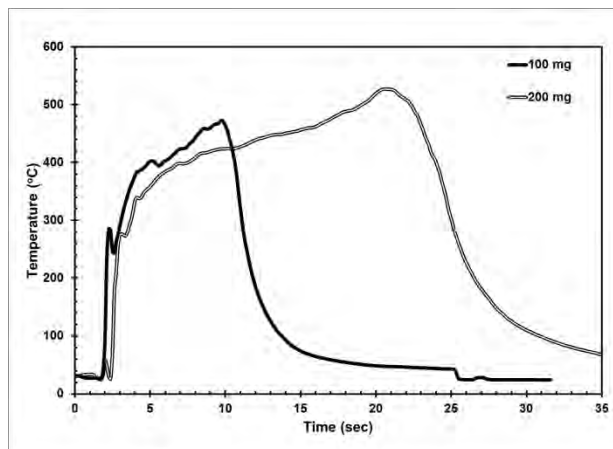
**Figure 3.1-4 SEM of middle layer of a multi-layer substrate showing capture of the 20-40 nm  $\text{Fe}_2\text{O}_3$  particles.**

The highest thermal responses were from those fabricated using 10 psi which was attributed to a higher porosity substrate. The thermal responses for those substrates were consistently above  $400^\circ\text{C}$  and sustained for an average of 7 seconds. In addition, vacuum filtered substrates (higher porosity) showed a maximum average thermal response of  $650^\circ\text{C}$  compared to the  $500$ - $550^\circ\text{C}$  from the pressure filtrated substrates. Presently substrates fabricated at lower filtration pressures are being characterized. Fabrication of substrates at lower filtration pressures can take several hours, therefore for the work herein described 20 psi was chosen as the optimal fabrication pressure.

For substrates fabricated at 20 psi a thermal response of greater than  $400^\circ\text{C}$  sustained for approximately 5 seconds was observed. It is desired to “tune” the time that the thermal response is sustained. For effective tuning we considered the addition of increased quantities of  $\text{Fe}_2\text{O}_3$  within the middle layer. As shown in Figure 3.2-2 there was only a moderate increase in the maximum combustion temperature observed but the overall burn time was increased from 5 seconds to 16 seconds.



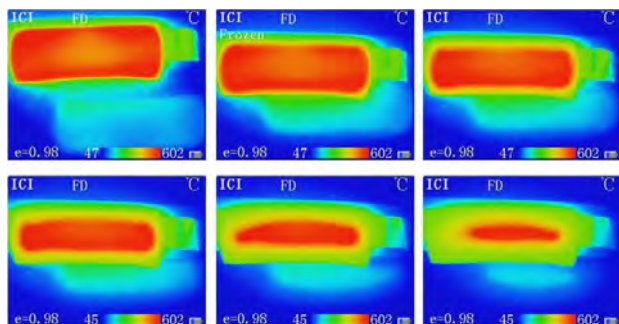
**Figure 3.2-1: Thermal response measured using IR pyrometer for substrates at different filtration pressures.**



**Figure 3.2-2: Thermal response of two substrates containing different amounts of iron oxide before reduction.**

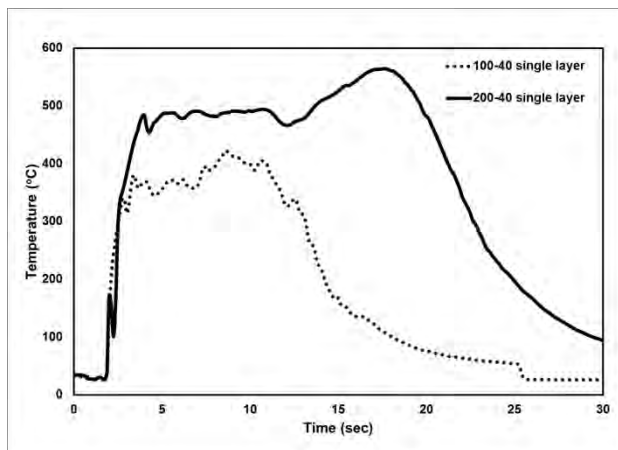
To ensure that the substrates were igniting and burning uniformly a thermal camera was used to record the thermal response of a substrate when exposed to ambient air. The thermal response of a multi-layer substrate with 200 mg of iron oxide is shown Figure 3.2-3.

The thermal camera records one image per second so the first image is recorded shortly after being removed and exposed to ambient air. Therefore, the rise time and burn time cannot be accurately measured using this characterization method; however, it does allow direct observation of the thermal profile over the entire substrate. As shown in Figure 3.2-3 the substrate ignites uniformly and cools from the exterior edges as expected.



**Figure 3.2-3: Thermal images of 3 layer substrate with 200 mg of iron oxide nanoparticles after reduction when exposed to ambient air.**

We now consider the single-layer substrates and compare their thermal responses to those of the multi-layer. With the single-layer substrates the total quantity of MWNTs was maintained at 40 mg and the quantity of  $\text{Fe}_2\text{O}_3$  was varied up to 200 mg. Forty milligrams of MWNTs was chosen based on the minimum quantity necessary to form a self-supporting substrate. As shown in Figure 3.2-4 we observed a reduction in the maximum temperature for the single-layered substrates because the particles were more dispersed within the layer. This was confirmed by increased addition of  $\text{Fe}_2\text{O}_3$  particles where the thermal response was increased to  $560^\circ\text{C}$  and as expected this resulted in an increase of 10 seconds for the burn time. What is of interest is that single-layer substrates appear to have a decreased rise time. Though at this time this is strictly qualitative, a more accurate method for accurately measuring the rise time is being investigated.

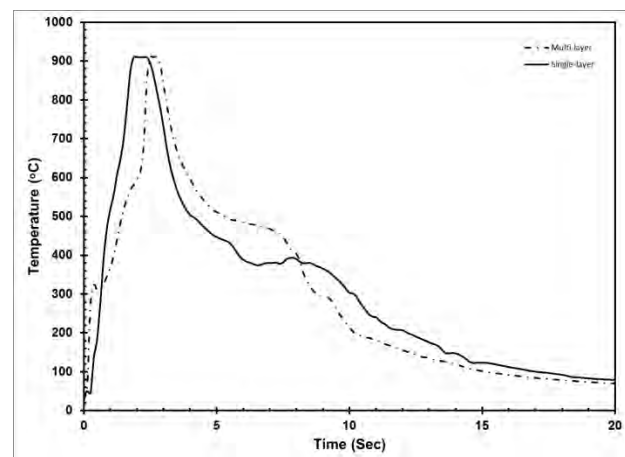


**Figure 3.2-4: Thermal response of single-layer substrates with 100 mg and 200 mg  $\text{Fe}_2\text{O}_3$ .**

### 3.2. THERMAL RESPONSE WITH ADDITION OF A SECONDARY FUEL

The second portion of this research was focused on the addition of a secondary fuel into the pyrophoric substrate. The addition of a secondary fuel allows for the thermal response of the substrates to be tuned both in maximum temperature but also sustenance. Secondary fuels that can be added include Al, Si, B, Mg, Co and  $\text{TiH}_2$ . Currently we have focused on addition of Al (80 nm and Valimet H2) and  $\text{TiH}_2$ . During the oxidation of the iron to iron oxide the heat generated is capable of initiating the secondary reaction. For Al the secondary reaction is a thermite reaction between the iron oxidation products and the aluminum; whereas for  $\text{TiH}_2$  the reaction is based on the decomposition and ignition of the  $\text{TiH}_2$ . Therefore we have two distinct cases to consider. 20 wt% Al was added to both multi-layer and single-layer substrates with 200mg  $\text{Fe}_2\text{O}_3$ . As shown in Figure 3.3-1 we observe an increase in the maximum temperature to over  $900^\circ\text{C}$  for both types of substrates. However, these temperatures are only maintained for 0.4 second for multi-layer and 0.7 second for single-layer substrates. With the presence of Al the maximum temperature is now driven by the thermite reaction and is sustained on the time scale representative of the thermite rather than strictly oxidation.

It is more clearly seen in this case that the rise time is reduced for single-layer substrates as shown by Figure 3.3-1.



**Figure 3.3-1: Thermal response of porous self-supporting substrates with the addition of a secondary fuel (20 wt% 80 nm Al).**

Preliminary experiments with  $\text{TiH}_2$  as the secondary fuel have shown maximum temperatures above  $900^\circ\text{C}$ .

### 4. SUMMARY AND FUTURE WORK

For the first time the fabrication of pyrophoric substrates using a bottom-up approach starting with nanosize iron oxide and multi-walled carbon nanotubes was demonstrated. It was observed that such substrates

possess adequate mechanical strength and they are pyrophoric when exposed to air. It was also demonstrated that MWNTs combined with alpha-iron and additional fuel in the form of metal (nano Al) or metal hydride particles increases the combustion temperature allowing for the thermal response of the substrates to be tuned.

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